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(54) **A powder coating composition.**

(57) A powder coating composition comprises as resinous components, a base resin having two or more oxirane groups in its molecule and an epoxy resin hardener; the composition being characterized by containing from 0.5 to 10% by weight based on the weight of the base resin, of a vinyl resin containing 1 to 10% by weight of units derived from one or more aliphatic dicarboxylic acids selected from thiomalic acid, maleic acid, fumaric acid and itaconic acid, the vinyl resin having a number average molecular weight of from 1000 to 8000 and a glass transition temperature of from -40°C to 100°C.

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The present invention relates to a powder coating and more specifically, a powder coating which is capable of resulting a cured coating being excellent in smoothness, gloss, image clarity and the like.

A powder coating is generally applied on a substrate by using a fluidized bed dip coating, an electrostatic coating, a powdering, a flame spray coating, a flock coating and the like and a number of powder coatings based on such resins as plasticized PVC, polyethylene, nylon, polyester, cellulose, epoxy resin, chlorinated polyether, polyurethane, fluorine, resin and the like, which are selected so as to be optimum for the selected application means, have been widely used.

Among them, vinyl resin is excellent in chemical resistance, abrasion resistance and electric properties and moreover, is less expensive and hence, is widely used in practice. Also, has been widely accepted a combination of an epoxy resin and such hardener as dicyandiamide, aromatic amine, amine complex, acid anhydride, phenol resin/ acid catalyst and the like, because of resulting a coating with excellent chemical resistance, toughness, adhesion, properties, weather resistance, thermal resistance, abrasion resistance and electric properties.

Such powder coatings are in general far superior to solvent type coating compositions in hygienic and air-pollution points of view and therefore getting more or more popular in coating area. However, since there remain problems in coating smoothness, gloss, image clarity and the like, they are in general not suitable as a top coat for automobile and the like and there are always longing for the improvement of such properties.

For this ends, various studies have been made. For example, in Japanese Patent Publication (unexamined) No. 864/81 and ibid 120666/84, has been proposed a thermosetting type powder coating comprising a vinyl copolymer being composed of glycidyl group containing vinyl monomer and phosphoric acid ester vinyl monomer and having a particular softening point and a specific number average molecular weight, and an aliphatic dibasic acid hardener; in Japanese Patent Publication (unexamined) No. 47456/81, a powder coating comprising, as main ingredients, a phosphor-containing vinyl polymer having crosslinkable functional groups and having a softening point of 70 to 150°C and a number average molecular weight of 2000 to 30000, and a hardener; and in Japanese Patent Publication (unexamined) No. 87471/82, a powder coating comprising a thermosetting type resinous composition containing 0.01 to 10% by weight of phosphor-containing polymeric additive.

However, they are all relied on phosphor-containing binder resin or phosphor-containing polymeric additive, and are still not in the mark in the intended objects and effects. There are also problems in respects of public hygiene and health, environmental air-pollution and the like because of the presence of phosphor component. Therefore, there are always demands for powder coatings which are not relied on or relied on the least quantities of phosphor-containing binder resin or additive, and which can be used as a top coat for automobile body and the like.

It is therefore, an object of the invention to provide a powder coating which is free from phosphor-containing polymer and is useful as a top coat for automobile body and the like, capable of resulting a cured coating with excellent smoothness, gloss, image clarity, weather resistance, and the like.

Summary of the invention

According to the present invention, the abovementioned object can be attained with A powder coating comprising a thermosetting type powder coating resinous composition comprising, as resinous components, a base resin having 2 or more oxirane groups in its molecule and a hardener for epoxy resin, which is characterized by being further added with a vinyl resin containing 1 to 10% by weight of at least one aliphatic dicarboxylic acid component selected from the group consisting of thiomalic acid, maleic acid, fumaric acid and itaconic acid and having a number average molecular weight of 1000 to 8000 and a glass transition temperature of -40° to 100°C, in an amount of 0.5 to 10% by weight of the powder coating.

In this invention, as a resinous vehicle of a thermosetting type powder coating, a combination of a base resin having 2 or more oxirane groups in its molecule and a hardening agent for epoxy resin is used.

As the base resin, the following may be satisfactorily used, providing having 2 or more oxirane groups.

(1) acrylic resin:

Copolymer comprising 20 to 50% by weight of other ethylenically unsaturated monomers and having a glass transition temperature of 30° to 75°C and a number average molecular weight of 1500 to 10000.

Examples of glycidyl group containing monomers are glycidyl acrylate, glycidyl methacrylate, methyl glycidyl acrylate, methyl glycidyl methacrylate, glycidyl ether of allyl alcohol, glycidyl ether of methallyl alcohol, methyl glycidyl ether of allyl alcohol, methyl glycidyl ether of methallyl alcohol, N-glycidyl acrylamide, vinyl sulfonic acid glycidyl and the like. They are used each alone or in the combination of 2 or more.

Other monomers to be copolymerized with said glycidyl group containing monomer are such members as being inert to said glycidyl group, i.e. being unable to react with said glycidyl group at a mixing or kneading

temperature, and capable of entering in the copolymerization with the abovementioned glycidyl group containing monomers are acrylates, methacrylates and other ethylenically unsaturated monomers. They are also used each singularly or in the combination of 2 or more.

Typical examples of such acrylates or methacrylates are methyl acrylate, ethyl acrylate, n-propyl acrylate, isopropyl acrylate, n-butyl acrylate, isobutyl acrylate, t-butyl acrylate, cyclohexyl acrylate, 2-ethyl hexyl acrylate, octyl acrylate, 2-ethyloctyl acrylate, dodecyl acrylate, benzyl acrylate, methyl methacrylate, ethyl methacrylate, n-propyl methacrylate, isopropyl methacrylate, n-butyl methacrylate, isobutyl methacrylate, t-butyl methacrylate, hexyl methacrylate, cyclohexyl methacrylate, 2-ethylhexyl methacrylate, octyl methacrylate, 2-ethyloctyl methacrylate, benzyl methacrylate, dodecyl methacrylate, phenyl methacrylate, 2-hydroxyethyl acrylate, 2-hydroxyethyl methacrylate, 2-hydroxypropyl acrylate, 2-hydroxypropyl methacrylate and the like.

Examples of other ethylenically unsaturated monomers are dialkyl fumarates as diethyl fumarate, dibutyl fumarate and the like; dialkyl itaconates as diethyl itaconate, dibutyl itaconate and the like; styrene, vinyl toluene, α -methyl styrene, acrylonitrile, methacrylonitrile, acrylamide, methacrylamide, methylol acrylamide, alkoxy methylolamide, vinyl oxazoline, vinyl acetate, vinyl propionate, lauryl vinyl ether and the like. They may be used each alone or in the combination of two or more.

(2) Polyester resins:

Conventional polyesters for coating use, modified to include epoxy groups and epoxy-containing polyester resins. Examples of polyhydric alcohol to be used in the preparation of such polyester resin are ethyleneglycol, propyleneglycol, neopentylglycol, 1,6-hexanediol, 1,3-butyleneglycol, 1,4-butyleneglycol, bis(hydroxyethyl)terephthalate, hydrogenated bisphenol A, trimethylol ethane, trimethylol propane, glycerin, pentaerythritol, 1,4-cyclohexane dimethanol or alkyleneoxide addition product thereof, and such epoxy compounds as Cardula E.

Examples of mono- and poly-basic carboxylic acids are phthalic acid, isophthalic acid, terephthalic acid, hexadecanoic acid, trimellitic acid, succinic acid, oxalic acid, adipic acid, sebacic acid, benzoic acid, p-t-butyl benzoic acid, p-hydroxy benzoic acid, acrylic acid, methacrylic acid, and their anhydrides, hydrogenated products or methyl esters. Introduction of epoxy group may be carried out in any conventional ways among them, addition of polyfunctional epoxy compound may be one of the most easiest ways.

(3) Epoxy resins:

Typical examples are monoepoxides as C_1 to C_8 -alkyl glycidyl ether, allyl glycidyl ether, phenyl glycidyl ether, styrene oxide, C_1 - C_4 alkylphenyl glycidyl ether, glycidyl versatate and the like; di- or poly-epoxides as C_4 - C_6 alkylene glycidyl ether type epoxy resin, bisphenol glycidyl ether type epoxy resin, bisphenol methyl glycidyl ether type epoxy resin, novolak type epoxy resin and the like; and epoxy esters obtained by the esterification of a part of epoxy groups in said di- or poly-epoxides with oil fatty acid, benzoic acid, acrylic acid or methacrylic acid. One or combination of two or more of said epoxy resins may be satisfactorily used.

In this invention, though it is not always necessary, but the abovementioned base resin may be modified with 0.05 to 10 % by weight, preferably 0.1 to 5 % by weight, of acid phosphate and used as a base resin.

Examples of such acid phosphates are methyl acid phosphate, isopropyl acid phosphate, butyl acid phosphate, dibutyl phosphate, monobutyl phosphate, 2-ethylhexyl acid phosphate, di-2-ethylhexyl phosphate, isodecyl acid phosphate, monoisodecyl phosphate, dodecyl acid phosphate, and the like. At that time, taking due consideration of dispersion properties, water resistance and the like of the powder coating, said acid phosphate should be controlled in a range of 0.05 to 10%, preferably 0.1 to 5%, of the base resin weight.

As a hardening agent for epoxy resin, amine compounds may be satisfactorily used, providing being solid at room temperatures and having comparatively low reactivities, and however, most preferable members are acid anhydrides, polybasic acids and the like. Examples are glutaric acid, adipic acid, pimelic acid, suberic acid, azelaic acid, sebacic acid, 1,12-dodecane diacid, 1,20-eicosane diacid, citric acid, maleic acid, citraconic acid, itaconic acid, glutaconic acid, phthalic acid, isophthalic acid, hexahydrophthalic acid, cyclohexene 1,2-dicarboxylic acid and the like. They may be acid anhydrides as succinic anhydride, sebacic anhydride, phthalic anhydride, itaconic anhydride, trimellitic anhydride and the like and may be polyesters having 2 or more carboxyl groups in molecule. In this invention, to a thermosetting type powder coating comprising the abovementioned base resin and the hardening agent, a particular amount of particular vinyl resin is added for the improvement in smoothness, gloss, image clarity and the like.

The present vinyl resin is characterized by containing as a constituting component, 1 to 10% by weight of aliphatic dicarboxylic acid selected from the group consisting of thiomalic acid, maleic acid, fumaric acid and itaconic acid, and having a glass transition temperature of -40° to 100°C and a number average molecular

weight of 1000 to 8000.

In the case of thiomalic acid, the defined amount of thiomalic acid are used as a polymerization regulator in the polymerization of vinyl monomers and said acid may be located at the end portion of the formed polymer chain.

5 In the case of maleic acid, fumaric acid or itaconic acid, such unsaturated acid may be used as a part of vinyl monomers, thereby incorporating said acid into the polymer chain structure.

Therefore, the present vinyl resin may be easily prepared by effecting polymerization of α , β -ethylenically unsaturated monomers with or without the abovementioned aliphatic unsaturated dicarboxylic acid in the presence of conventional polymerization catalyst and polymerization regulator, whose glass transition temperature
10 may be freely controlled by the kind and amount ratio of the monomers used and number average molecular weight by the polymerization conditions and selection of polymerization regulator.

However, in this invention, it is essential that the content of said aliphatic dicarboxylic acid in the vinyl resin be in a range of 1 to 10% by weight of the total resin.

Though the exact reasons why the presence of such acid in the vinyl resin is contributive toward the marked improvements in smoothness, gloss and image clarity of the cured coating are not yet clear, but the inventors
15 are of the opinion that on one hand, the vinyl resin itself will become an integral part of the cured coating resin through the reaction of said acid groups in the curing reaction of the powder coating, and on the other hand, the vinyl resin may be localized, as in the case of surfactant, at the coating surface due to the polarity and non-polarity of the acid groups of dicarboxylic acid and main chain of the vinyl resin, thereby contributing to the
20 improvements in smoothness, gloss and image clarity of the cured coating.

In any way, in this invention, particular amount of said particular acid should be present in the vinyl resin. This is because, if the acid content is less than 1% by weight, it is unable to expect the desired effects and if the said content exceeds over the upper limit of 10% by weight, there is indeed the desired improvement in coating appearance, but there are undesired loss in weather resistance, impact strength and the like.

25 The glass transition temperature of the vinyl resin is also important in this invention, as well as a number average molecular weight thereof.

If the glass transition temperature is lower than -40°C , there is a tendency that weather resistance and impact strength of the coating be lowered, whereas if it exceeds over 100°C , there is a considerable loss in coating appearance. If the number average molecular weight of the vinyl resin is less than 1000, there is a decrease in impact strength and if it exceeds over 8000, there is a marked loss of coating appearance. Therefore,
30 the present vinyl resin should have a glass transition temperature of -40° - 100°C and a number average molecular weight of 1000-8000, and preferably 2000-6000.

In this invention, such properties as smoothness, gloss, image clarity and the like of the cured coating are greatly improved by the inclusion of such vinyl resin in a thermosetting type resinous composition comprising
35 as main ingredients, a base resin and a hardening agent, in an amount of about 0.5 to 10% by weight, and preferably 1 to 5% by weight of the base resin weight. If the said amount is less than 0.5%, it is unable to expect the desired effects of the vinyl resin, and if it exceeds over 10% by weight, there are undesired loss in weather resistance, impact strength and other coating properties.

The vinyl resin may be added to the powder coating composition at any stage in the preparation of powder
40 coating up to the melt dispersion of the said coating composition.

The powder coating may be either clear or colored composition. Any of the conventional additives may be satisfactorily used in this powder coating.

Examples are inorganic or organic pigments customarily used in such powder coating.

45 Typical examples of inorganic pigments are zinc oxide, carbon black, titanium oxide, antimony white, black iron oxide, red iron oxide, red lead, cadmium yellow, zinc sulfide, lithopone, barium sulfate, lead sulfate, barium carbonate, white lead, alumina white and the like.

Typical examples of organic pigments are azo pigments poly condensation azo pigments metal complex azo pigments, benzimidazolone pigments, phthalocyanine pigments (blue, green), thioindigo pigments, anthraquinone pigments, flavanthrone pigments, indanthrene pigments, anthrapyridine pigments, pyranthrone pigments, isoindolinone pigments, perylene pigments, perinone pigments and quinacridone pigments. However,
50 there are only of illustrative and various other pigments customarily used may be successfully employed.

The present powder coating may be added with other conventional additives, as desired, including various resins as epoxy resin, polyester resin, polyamide resin, cellulose derivatives and the like; pigments, flow regulator, anti-blocking agent, ultra violet rays absorber, benzoin, antistatic agent, antioxidant and the like.

55 The present powder coating may be advantageously prepared by pre-mixing the essential three components of the abovementioned base resin, hardening agent and vinyl resin, together with other optional components as various resins, pigments, flow regulator, anti-blocking agent, UV absorber, benzoin, antistatic agent, antioxidant or the like, melt-mixing by means of heat roll, extrude and other mixing machine, cooling the melt

and pulverizing the solid mass.

The present powder coating may be applied on a substrate by using a conventional coating method as, for example, electrostatic spraying, fluidization dip coating and the like and thus applied coating is usually baked in a baking furnace maintained at 150°-210°C to obtain a cured coating.

Thus obtained coating is far superior to the conventional coatings in respects of coating smoothness, gloss and image clarity and hence, the present powder coating is specifically useful for the coating of automobile bodies and the like.

The present invention shall be now more fully explained in the following Examples. Unless otherwise being stated, all parts and percentages are by weight.

10

Reference Example 1

Preparation of acrylic resin

Into a flask fitted with a dropping funnel, a stirrer and a thermometer, were placed 95 parts of xylene and heated to 130°C. To this, was dropwise added from the dropping funnel a mixture of 25 parts of styrene, 27 parts of methyl methacrylate, 30 parts of glycidyl methacrylate and 4 parts of Kayaester O (initiator) in 3 hours. After completion of said addition, the content was maintained at the same temperature for 30 minutes and then a mixture of 4 parts of xylene and 0.4 part of Kayaester O was dropwise added in 1 hour. Thereafter, the combined was maintained at 130°C for 2 hours and xylene was distilled off under reduced pressure to obtain an acrylic resin A.

20

Reference Example 2

Preparation of acrylic resin

Into a flask fitted with a dropping funnel, a stirrer and a thermometer, were placed 95 parts of xylene and heated to 130°C. To this, was dropwise added from the dropping funnel a mixture of 20 parts of styrene, 34 parts of methyl methacrylate, 30 parts of glycidyl methacrylate, 10 parts of n-butyl methacrylate and 4 parts of Kayaester O (initiator) in 3 hours. After completion of said addition, the content was maintained at the same temperature for 30 minutes and then a mixture of 4 parts of xylene and 0.4 part of Kayaester O was dropwise added in 1 hour. Thereafter, the combined was maintained at 130°C for 2 hours, dropwise added with a mixture of 3 parts of butyl acid phosphate and 10 parts of xylene at 130°C in 1 hour and then xylene was distilled off under reduced pressure to obtain an acrylic resin B.

30

35

Reference Examples 3 - 4

Preparation of acrylic resins

Following the procedures of Reference Example 2 and using the materials shown in Table 1, acrylic resins C and D were prepared, respectively.

40

Reference Examples 5 - 8

Preparation of levelling agents

Following the procedures of Reference Example 1 and using the materials shown in Table 1, levelling agents E, F, G and H were prepared, respectively.

Example 1

Preparation of acryl powder coating

100 parts of the acrylic resin A, 24 parts of decane dicarboxylic acid, and 2 parts of levelling agent E were dry-mixed in Henshel Mixer and then subjected to melt dispersion at 100°C by using Co-kneader PR-46 (trademark, Bus Co., Swiss). After cooling, the solid mass was pulverized in Hammer Mill and shieved through 150 mesh wire net to obtain an acryl powder coating.

55

Thus obtained powder coating was applied on a steel plate by electrostatic spraying and baked at 160°C

for 20 minutes to obtain a cured coating (about 80 μ thickness). Appearance and impact strength of thus obtained coating were examined and the test results were shown in Table 2. Appearance was excellent.

Example 2

Preparation of acryl powder coating

100 parts of the acrylic resin B, 24 parts of decane dicarboxylic acid, 30 parts of titanium oxide CR 50 (trademark of Ishihara Sangyo) and 2 parts of levelling agent E were dry-mixed in Henshel Mixer (trademark of Mitui Miike Seisakusho) and then subjected to melt dispersion at 100°C by using Co-kneader PR-46 (trademark, Bus Co., Swiss). After cooling, the solid mass was pulverized in Hammer Mill and shieved through 150 mesh wire net to obtain an acryl powder coating.

Thus obtained powder coating was applied on a steel plate by electrostatic spraying and baked at 160°C for 20 minutes to obtain a cured coating (about 80 μ thickness). Appearance and impact strength of thus obtained coating were examined and the test results were shown in Table 2. Appearance was excellent.

Examples 3 to 5

Preparation of acryl powder coatings

Following the procedures of Example 2 and using the materials shown in Table 2, various acryl powder coatings were prepared.

Each of thus obtained powder coating was applied on a steel plate by electrostatic spraying and baked at 160°C for 20 minutes to obtain a cured coating (about 80 μ thickness). Appearance and impact strength of thus obtained coating were examined and the test results were shown in Table 2. Appearance was excellent, in each case.

Example 6

Preparation of polyester powder coating

Into a flask fitted with a dropping funnel, a stirrer and a thermometer, were placed 100 parts of ER 6610 (trademark, polyester resin, manufactured by Nippon Polyester Co., Ltd.) and 5 parts of bi-functional Epoxy ERL-4234 (Union Carbide Co.) and the mixture was heated at 120°C for 1 hour and then cooled.

105 parts of the polyester resin thus obtained, 3 parts of the levelling agent E, 36 parts of Kurelan UI (blocked isocyanate, trademark, BASF) and 40 parts of titanium oxide CR 50 were dry-mixed in Henshel Mixer (trademark of Mitui Miike Seisakusho) and then subjected to melt dispersion at 100°C by using Co-kneader PR-46 (trademark, Bus Co., Swiss). After cooling, the solid mass was pulverized in Hammer Mill and shieved through 150 mesh wire net to obtain a powder coating.

Thus obtained powder coating was applied on a steel plate by electrostatic spraying and baked at 180°C for 20 minutes to obtain a cured coating (about 80 μ thickness). Appearance and impact strength of thus obtained coating were examined and the test results were shown in Table 2. Appearance was excellent.

Example 7

Preparation of epoxy powder coating

100 parts of Epotohto YD-014 (trademark, epoxy resin, manufactured by Tohto Kasei), 2 parts of the levelling agent F, 3 parts of dicyandiamide and 40 parts of titanium oxide CR 50 were dry-mixed in Henshel Mixer (trademark of Mitui Miike Seisakusho) and then subjected to melt dispersion at 100°C by using Co-kneader PR-46 (trademark, Bus Co., Swiss). After cooling, the solid mass was pulverized in Hammer Mill and shieved through 150 mesh wire net to obtain a powder coating.

Thus obtained powder coating was applied on a steel plate by electrostatic spraying and baked at 180°C for 20 minutes to obtain a cured coating (about 80 μ thickness).

Appearance and impact strength of thus obtained coating were examined and the test results were shown in Table 2. Appearance was excellent.

Comparative Example 1

Preparation of acryl powder coating

5 100 parts of the acrylic resin A and 24 parts of decane dicarboxylic acid were dry-mixed in Henshel Mixer(trademark of Mitui Miike Seisakusho) and then subjected to melt dispersion at 100°C by using Co-kneader PR-46 (trademark, Bus Co., Swiss). After cooling, the solid mass was pulverized in Hammer Mill and shieved through 150 mesh wire net to obtain an acryl powder coating.

10 Thus obtained powder coating was applied on a steel plate by electrostatic spraying and baked at 160°C for 20 minutes to obtain a cured coating (about 80 μ thickness). Appearance and impact strength of thus obtained coating were examined and the test results were shown in Table 3. Appearance was no good.

Comparative Example 2

15 Preparation of acryl powder coating

100 parts of the acrylic resin B, 24 parts of decane dicarboxylic acid and 30 parts of titanium oxide CR 50 (Ishihara Sangyo) were dry-mixed in Henshel Mixer(trademark of Mitui Miike Seisakusho) and then subjected to melt dispersion at 100°C by using Co-kneader PR-46 (trademark, Bus Co., Swiss). After cooling, the solid mass was pulverized in Hammer Mill and shieved through 150 mesh wire net to obtain an acryl powder coating.

20 Thus obtained powder coating was applied on a steel plate by electrostatic spraying and baked at 160°C for 20 minutes to obtain a cured coating (about 80 μ thickness).

Appearance and impact strength of thus obtained coating were examined and the test results were shown in Table 3. Appearance was no good.

25 Comparative Examples 3 to 6

Preparation of acryl powder coatings

30 Following the procedures of Example 2 and using the materials shown in Table 3, various acryl powder coatings were prepared.

Each of thus obtained powder coating was applied on a steel plate by electrostatic spraying and baked at 160°C for 20 minutes to obtain a cured coating (about 80 μ thickness). Appearance and impact strength of thus obtained coating were examined and the test results were shown in Table 2. Appearance was no good in each case.

Comparative Example 7

Preparation of polyester powder coating

40 Into a flask fitted with a dropping funnel, a stirrer and a thermometer, were placed 100 parts of ER 6610 (trademark, polyester resin, manufactured by Nippon Polyester Co.,Ltd.) and 5 parts of bi-functional Epoxy ERL-4234 (Union Carbide Co.) and the mixture was heated at 120°C for 1 hour and then cooled.

105 parts of the polyester resin 1 thus obtained, 3 parts of the levelling agent E, 36 parts of Kurelan UI- (blocked isocyanate, trademark, BASF) and 40 parts of titanium oxide CR 50 were dry-mixed in Henshel Mixer(trademark of Mitui Miike Seisakusho) and then subjected to melt dispersion at 100°C by using Co-kneader PR-46 (trademark, Bus Co., Swiss). After cooling, the solid mass was pulverized in Hammer Mill and shieved through 150 mesh wire net to obtain a powder coating.

50 Thus obtained powder coating was applied on a steel plate by electrostatic spraying and baked at 180°C for 20 minutes to obtain a cured coating (about 80 μ thickness). Appearance and impact strength of thus obtained coating were examined and the test results were shown in Table 3. Appearance was no good.

Comparative Example 8

55 Preparation of epoxy powder coating

100 parts of Epotohto YD-014 (trademark, epoxy resin, manufactured by Tohto Kasei), 2 parts of the levelling agent F, 3 parts of dicyandiamide and 40 parts of titanium oxide CR 50 were dry-mixed in Henshel

Mixer(trademark of Mitui Miike Seisakusho) and then subjected to melt dispersion at 100°C by using Co-kneader PR-46 (trademark, Bus Co., Swiss). After cooling, the solid mass was pulverized in Hammer Mill and shieved through 150 mesh wire net to obtain a powder coating.

Thus obtained powder coating was applied on a steel plate by electrostatic spraying and baked at 180°C for 20 minutes to obtain a cured coating (about 80 μ thickness).

Appearance and impact strength of thus obtained coating were examined and the test results were shown in Table 3. Appearance was no good .

Evaluation Methods:

1) Appearance (smoothness)

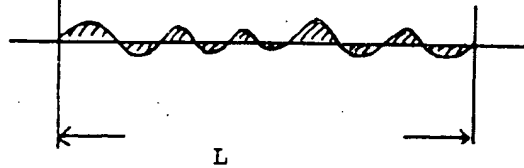
(1) visual examination

- good
- △ fairly no good
- × no good

(2) Ra (roughness of surface center)

Surface roughness meter was used. Coating thickness: 80.

$$Ra = S/L$$



wherein L stands for length and S is the total area of the oblique line portion
Roughness is increased in proportion to the increase in Ra value .

2) Impact strength:

1/2 inch hard ball with 500 g weight was dropped from various hights perpendicularly onto the coated plate and tolerable hight withoutn damage was measured. Impact strength was expressed by this hight(cm).

Table 1(1)

Ref. Example	1	2	3	4
acrylic resin	A	B	C	D
5 Solvent xylene	95	95	95	95
Monomers				
10 Styrene	25	20	20	20
methyl methacrylate	27	34	38	9
15 glycidyl methacrylate	30	30	30	30
n-butyl methacrylate	-	16	-	41
20 2-ethyl hexyl methacrylate	18	-	10	-
25 2-hydroxyethyl methacrylate	-	-	2	-
thiomalic acid	-	-	-	-
maleic acid	-	-	-	-
30 Initiator 1st AIBN	-	-	-	-
KayaEsterO	4	4	4	4
35 Initiator 2nd AIBN	-	-	-	-
KayaEsterO	0.4	0.4	0.4	0.4
40 xylene	4	4	4	4
acid phosphate butyl acid phosphate	-	3	-	-
45 ethyl acid phosphate	-	-	5	20
50 resin characteristics glass trans temp.	50	60	60	40
55 number average molec-weight	4000	4000	4000	4000

Table 1(2)

Ref. Example	5	6	7	8
levelling agent	E	F	G	H
Solvent xylene	95	95	95	95
Monomers	-	-	-	-
Styrene				
methyl methacrylate	75	1	8	-
glycidyl methacrylate	-	-	-	-
n-butyl methacrylate	19	80	70	70
2-ethyl hexyl methacrylate	-	16	-	8
2-hydroxyethyl methacrylate	6	-	2	18
thiomalic acid	3	5	-	-
maleic acid	-	-	20	4
Initiator 1st				
AIBN	0.5	0.5	-	-
KayaEsterO	-	-	2.5	0.5
Initiator 2nd				
AIBN	0.05	0.05	-	-
KayaEsterO	-	-	0.5	0.05
xylene	5	4	4	4
acid phosphate				
butyl acid phosphate	-	-	-	-
ethyl acid phosphate	-	-	-	-
resin				
characteristics				
glass trans temp.	80	30	100	35
number average				
molec-weight	4000	2000	6000	20000

Table 2(1)

	Ex.1	Ex.2	Ex.3	Ex.4
	acryl clear coat.comp.	acryl coat.comp.	acryl coat.comp.	acryl coat.comp.
acryl resin A	100	-	100	-
acryl resin B	-	100	-	100
acryl resin C	-	-	-	-
acryl resin D	-	-	-	-
ER 6610 1)	-	-	-	-
YD-014	-	-	-	-
levelling agent E	2	2	-	-
levelling agent F	-	-	4	4
levelling agent G	-	-	-	-
levelling agent H	-	-	-	-
CR 50	-	30	30	30
DDA	24	24	24	24
dicyandiamide	-	-	-	-
kureran UI	-	-	-	-
Appearance visnal	○	○	○	○
Ra	0.8	0.9	0.9	0.9
Properties impact	40<	40<	40<	40<

1) polyester resin 1

Table 2(2)

	Ex.5	Ex.6	Ex.7
	acryl coat.comp.	polyester coat.comp.	epoxy coat.comp.
5			
	acryl resin A	-	-
10	acryl resin B	-	-
	acryl resin C	100	-
	acryl resin D	-	-
15	ER 6610	105	-
	YD-014	-	100
	levelling agent E	3	-
20	levelling agent F	4	2
	levelling agent G	-	-
	levelling agent H	-	-
	CR 50	30	40
25	DDA	24	-
	dicyandiamide	-	3
	kureran UI	36	-
30	Appearance visnal	○	○
	Ra	0.9	1.0
35	Properties impact	40 <	40 <

Table 3(1)

Comp.Ex.	1	2	3	4
acryl resin A	100	-	-	100
acryl resin B	-	100	-	-
acryl resin C	100	100	-	-
acryl resin D	-	-	100	-
ER 6610 1)	-	-	-	-
YD-014	-	-	-	-
levelling agent E	-	-	2	-
levelling agent F	-	-	-	-
levelling agent G	-	-	-	3
levelling agent H	-	-	-	-
CR 50	-	30	30	30
DDA	24	24	24	24
dicyandiamide	-	-	-	-
kureran UI	-	-	-	-
Appearance visnal	△	△	△	△
Ra	1.2	1.4	1.1	1.2
Properties impact	> 40	10	10	30

1) polyester resin

Table 3(2)

Comp.Ex.	5	6	7	8
acryl resin A	100	-	-	-
acryl resin B	-	100	-	-
acryl resin C	-	-	-	-
acryl resin D	-	-	-	-
ER 6610 1)	-	-	105	-
YD-014	-	-	-	100
levelling agent E	-	20	3	-
levelling agent F	-	-	-	2
levelling agent G	-	-	-	-
levelling agent H	4	-	-	-
CR 50	30	30	40	40
DDA	24	24	-	-
dicyandiamide	-	-	-	3
kureran UI	-	-	36	-
Appearance visnal	Δ	Δ	\times	\times
Ra	1.1	1.2	1.4	1.4
Properties impact	25	10	> 40	> 40

1) polyester resin

Claims

1. A thermosetting powder coating composition comprising, as resinous components, a base resin having two or more oxirane groups in its molecule and an epoxy resin hardener; the composition being characterized by containing from 0.5 to 10% by weight based on the weight of the base resin, of a vinyl resin containing 1 to 10% by weight of units derived from one or more aliphatic dicarboxylic acids selected from thiomalic acid, maleic acid, fumaric acid and itaconic acid, the vinyl resin having a number average molecular weight of from 1000 to 8000 and a glass transition temperature of from -40°C to 100°C.
2. A powder coating composition according to claim 1, wherein the base resin is an acrylic resin, polyester resin, epoxy resin or derivative thereof modified with 0.05-10% by weight of an acid phosphate.
3. A powder coating composition according to claim 1 or claim 2, wherein the base resin is an acrylic resin obtained by the copolymerization of 20-50% by weight of glycidyl group containing monomer and 80-50% by weight of other co-polymerizable, α,β -ethylenically unsaturated monomers, and having a glass transition temperature of from 30°C-75°C and a number average molecular weight of from 1500-10000.



European Patent
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EUROPEAN SEARCH REPORT

Application Number

EP 91305913.5

DOCUMENTS CONSIDERED TO BE RELEVANT			EP 91305913.5
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl.5)
X	DATABASE WPIL, NO. 83-10 593 DERWENT PUBLICATIONS LTD., London * Abstract * & JP-A-57 205 458 (DNIN) 16-12-1982	1	C 09 D 5/03 C 09 D 163/00
A	DATABASE WPIL, NO. 88-358 606 DERWENT PUBLICATIONS LTD., London * Abstract * & JP-A-63 270 772 (NIOF) 08-11-1988	1	
			TECHNICAL FIELDS SEARCHED (Int. Cl.5)
			C 09 D 5/00 C 09 D 163/00 C 09 D 133/00 C 09 D 167/00
The present search report has been drawn up for all claims			
Place of search VIENNA		Date of completion of the search 07-10-1991	Examiner PAMMINGER
CATEGORY OF CITED DOCUMENTS X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons & : member of the same patent family, corresponding document			

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